NATIONAL
WATER
RESEARCH
INSTITUTE

INSTITUT
NATIONAL
de RECHERCHE
sur les
EAUX

NWRI CONTRIBUTION 89-125

GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC DETERMINATION OF SOME RESIN AND FATTY ACIDS IN PULPMILL EFFLUENTS AS THEIR PENTAFLUOROBENZYL ESTER DERIVATIVES

by

Hing-Biu Lee[1], Thomas E. Peart[1]
and John M. Carron[2]

[1]Research and Applications Branch
National Water Research Institute
[2]National Water Quality Laboratory
Inland Waters Directorate
Canada Centre for Inland Waters
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario, Canada L7R 4A6

June 1989

MANAGEMENT PERSPECTIVE

The toxicity of pulpmill wastes to fish has long been established. Among the toxic constituents in effluents, resin acids are known as the major contributors of the toxicity since they are present at high concentrations and have similar toxicity as the chlorinated phenolics. In the past, the analytical methodology employed for the determination of resin acids and a few other fatty acids has not been sensitive enough for many monitoring applications such as the measurement of final effluents discharging into the environment. We have now developed an analytical method for these acids which is about 100 times more sensitive than the existing methodology.

Dr. J. Lawrence
Director, Research and Applications Branch

PERSPECTIVE - GESTION

La toxicité des déchets des usines de pâte est établie depuis longtemps. Parmi les éléments toxiques de ces effluents, les acides résiniques sont reconnus comme étant ceux qui contribuent le plus à la toxicité étant donné leur forte concentration et leur toxicité semblable à celles des composés phénoliques chlorés. Jusqu'à présent, la méthode analytique utilisée pour le dosage des acides résiniques et de quelques autres acides gras n'était pas assez sensible pour plusieurs applications de surveillance comme la mesure des effluents finals évacués dans l'environnement. Nous avons maintenant mis au point une méthode analytique pour ces acides, environ 100 fois plus sensible que la méthode existante.

J. Lawrence

Directeur, Direction de la recherche et des applications

SUMMARY

A sensitive gas chromatographic method for the determination of resin and fatty acids commonly found in pulpmill effluents is presented. The acids are extracted from effluent samples at pH 8 by methyl tert.-butyl ether and converted into their respective pentafluorobenzyl ester derivatives. After silica gel column cleanup, sample extracts are analyzed by GC with an electron capture detector using a 30 m DB-17 column. Mass spectral data of these esters obtained under electron impact and electron capture negative ion chemical ionization conditions are also described. The abundant and characteristic $(M-181)^-$ ions are used for the identification and quantitation of resin and fatty acids using a selected ion monitoring technique. Using an effluent with a low blank, spiked recovery of a mixture of 15 acids at 1000, 100, and 10 µg/L levels is quantitative. Based on a 25 mL sample and a concentration factor of 10, the method detection limit is 1 µg/L for all acids. Application of this procedure to some Canadian pulpmill samples is also presented.

RÉSUMÉ

Le présent ouvrage présente une méthode sensible de chromatographie en phase gazeuse pour le dosage des acides résiniques et des acides gras que l'on trouve normalement dans les effluents des usines de pâte. Les acides sont extraits des échantillons des effluents à un pH de 8 à l'aide de méthyl-t-butyléther et convertis en leurs dérivés ester de type pentafluorobenzyle respectifs. Après nettoyage sur colonne de gel de silice, les extraits de l'échantillon sont analysés par CPG à l'aide d'un détecteur à capture d'électrons dans une colonne DB-17 de 30 m. Les données de l'analyse par spectre de masse de ces esters obtenues dans des conditions d'ionisation chimique des ions négatifs et d'impact et de capture des électrons sont également décrites. Les ions $(M-181)^-$ abondants et caractéristiques sont utilisés pour l'identification et la quantification des acide résiniques et des acides gras à l'aide d'une technique choisie de surveillance ionique. L'utilisation d'un effluent avec un faible taux de récupération des blancs enrichis d'un mélange de 15 acides à des teneurs de 1000, 100 et 10 ug/L est quantitative. D'après un échantillon de 25 mL et un facteur de concentration de 10, la limite de détection de la méthode est de 1 ug/L pour tous les acides. On y présente également l'application de ce procédé aux échantillons de certaines usines canadiennes de pâte.

1.0 INTRODUCTION

Diterpene resin acids are major constituents of rosin and are naturally occurring in the bark of many softwood species such as spruce and pine. During the debarking process of logs, these acids are dissolved and discharged into the environment in the form of pulpmill effluents. Resin acids of concentrations as high as mg/L have been reported in bleached kraft, sulfite, and thermomechanical pulping effluents [1]. In general, hardwood effluents contain lower levels of resin acids than softwood effluents. These acids and, to a smaller extent, the unsaturated fatty acids also derived from woodroom effluents, have been identified as the major contributors to the toxicity of effluents to fish [2-5]. The 96-hr LC50 values of the common resin acids for salmon or rainbow trout (Table 1), are similar to those of chlorinated guaiacols and catechols found in bleached kraft effluents [6,7].

Recently, a paper on the direct gas chromatographic analysis of underivatized resin acids in gum rosin on a non-polar fused-silica capillary column has been reported [8]. However, most of the analyses of these resin and fatty acids (RFA) in pulpmill effluents were done on their methyl esters by gas chromatography with flame ionization detection [9]. Although this procedure is routinely used, it lacks the sensitivity required for many environmental samples. An alternative and potentially more sensitive technique for the analysis of these methyl esters using electron impact gas chromatography mass spectrometry (EI-GC-MS) has also been reported [10].

Pentafluorobenzyl (PFB) derivatives of many acidic phenoxy herbicides [11] and phenols [12] have been well characterized. Applications of the PFB derivatives to the determination of above pollutants in environmental samples were also documented [13-15]. Since the electron capture detector (ECD) is highly sensitive to the pentafluoro compounds, formation of such derivatives would greatly improve the detection limit of the non-halogenated acids such as the fatty acids and the majority of the resin acids. Application of electron capture negative ion chemical ionization mass spectrometry (EC-NICI-MS) has been successfully demonstrated in the analyses of the PFB and other electron capturing derivatives of chlorophenols [16,17] and chloroanilines [17] as well as some fluorinated derivatives of pesticides [18]. In these cases, strong yet characteristic ions were used in the quantitation and confirmation of the organics. EC-NICI-MS is, therefore, a potentially powerful tool for the analysis of the RFA PFB esters.

In this paper, we describe a sensitive and selective gas chromatographic (GC) method for the determination of the more commonly found RFA in pulpmill effluents by the formation of their PFB esters. The gas chromatographic resolution of these derivatives on capillary columns of three different stationary phases is discussed. The mass spectrometric data of the ester derivatives obtained under electron impact and negative ion chemical ionization modes are also presented. Application of this procedure to Canadian pulpmill effluents is also briefly described. A list of the selected RFA discussed in this paper is given in Table 1.

2.0 EXPERIMENTAL

2.1 Reagent and chemicals

All resin acids of purity from 85 to 99+ % (Table 1) were obtained from Helix-Biotech Scientific Ltd. (Vancouver, B.C., Canada) and used without further purification. It should be noted that chlorodehydroabietic acid was supplied in the form of an approximate 1:1 mixture of the 12- and 14-chlorodehydroabietic acids and the dichlorodehydroabietic acid was the 12,14-dichloro isomer. Palmitic, heptadecanoic, stearic, oleic, linoleic, linolenic, and tricosanoic acids, and pentafluorobenzyl bromide (PFBBr) were acquired from Aldrich Chemical Co. (Milwaukee, WI, USA).

Stock solutions of individual RFA of 1000 µg/mL were prepared in distilled-in-glass grade methyl tert.-butyl ether (Burdick and Jackson, Muskegon, MI, USA) and kept at 4°C in the dark. A mixture of the RFA each at 20 µg/mL was also prepared in the same solvent.

A PFBBr solution was prepared by dissolving 1 g of the reagent in 20 mL of acetone. A 30% (w/v) potassium carbonate solution was made by dissolving 3 g of the anhydrous base in 10 mL of water. All other solvents used were of distilled-in-glass grade.

2.2 Sampling of effluent samples

Grab effluent samples were collected in 100 mL brown screw capped bottles with aluminum foil liners. After adjustment of their pH to about 8 by dropwise addition of 1N KOH or HCl, these samples were kept at 4°C in the dark until analysis.

2.3 Extraction and derivatization of RFA

An aliquot of 2.5 µg of tricosanoic acid in 100 µL of methyl tert.-butyl ether (MTBE) was added to a 25 mL effluent sample at pH 8. The sample was extracted twice with 50 mL aliquots of MTBE for 30 min. each. After the extractions, the combined ethereal extracts were passed through a 5 cm column of anhydrous sodium sulfate contained in a 4 cm I.D. Allihn funnel. Using a rotary evaporator and a water bath of 40°C, the solvent was evaporated to near dryness and the residues were redissolved in three mL of acetone and transferred to a test tube. The volume of acetone was further reduced to 0.5 mL under a gentle stream of nitrogen. PFB ester derivatives of RFA were prepared by heating the above sample extract in acetone with 100 µL of the PFBBr reagent and 30 µL of the 30% potassium carbonate solution at 60°C for 30 min. in a tightly capped test tube. At the end of the reaction, the mixture was evaporated to dryness and the residues were redissolved in 2 mL of petroleum ether (PE, b.p. 30-60°C).

2.4 Column cleanup

The extracts were applied to a 5.00 g 5% deactivated silica gel column prewashed with 20 mL of PE. The column was then eluted with 50 mL of 5% (v/v) dichloromethane (DCM) in PE and this fraction was discarded. The PFB esters of the RFA were quantitatively eluted from the column by 75 mL of 25% (v/v) DCM in PE. This fraction, after solvent replacement with iso-octane and adjustment to a final volume of 2.5 mL, was ready for final GC analysis.

2.5 Calibration standard

Known amounts of RFA were directly derivatized and cleaned up as described above alongside the effluent samples and used as external standards for the quantitation of the acids.

2.6 Instrumentation

For gas chromatography-electron capture detection (GC-ECD), a Hewlett-Packard 5880A gas chromatograph equipped with split-splitless injectors and J&W DB-17 and DB-5 fused silica capillary columns was used. For gas chromatography-mass selective detection (GC-MSD), a Hewlett-Packard 5880A gas chromatograph equipped with a 5970B mass selective detector with data system and a Supelco SPB-5 column was used. In the case of EC-NICI work, a Finnigan 4500 gas chromatograph/ mass spectrometer with a Super INCOS data system and a J&W DB-1 column were used. All injections were done in the splitless mode and 2 µL of the sample were injected.

2.7 Chromatographic conditions

ECD analysis. Two 30 m x 0.25 mm I.D. x 0.25 µm capillary columns, DB-5 and DB-17, by J & W Scientific Co. were used. The initial oven temperature was set at 70°C with a 0.75 min hold. It was then programmed to 210°C at a rate of 30°C/min and then to 290°C at 2°C/min. The final temperature was further held for 15 min. The injection port and detector temperature were 250°C and 300°C,

respectively. Carrier gas was helium and column head pressure was 105 kPa.

MSD analysis. A 30 m x 0.25 mm I.D. x 0.25 µm Supelco SPB-5 capillary column was used. The temperature program as described for ECD work was used. Injection port and interface temperatures were 250°C and 280°C, respectively. Carrier gas was helium and column head pressure was 28 kPa.

EC-NICI-MS analysis. A 30 m x 0.32 mm I.D. x 0.25 µm J&W DB-1 capillary column was used. The oven temperature was set and held at 80°C for two minutes. It was programmed to 140°C at a rate of 10°C/min and then to 280°C at 6°C/min. The final temperature was held for another 10 min. The manifold, ion source, and transfer line temperatures were 100°C, 50°C and 250°C, respectively. Carrier gas was helium and column head pressure was 70 kPa. The reagent gas, hydrogen, was added as a makeup to pressurize the ion volume to ca. 0.8 torr.

2.8 Acquisition of mass spectral data

Full scan electron impact (EI) MS data were obtained by scanning the Hewlett-Packard MSD from m/z 50 to 560 at a rate of 0.82 scans/s and a scan threshold of 1000. The electron energy and electron multiplier voltage were 70 eV and 2000 V, respectively. For EC-NICI-MS (Finnigan) experiments, full scan data were obtained by scanning the above mass range in 1.5 s. In the case of selected ion monitoring (SIM) work, the $(M-181)^-$ ions of the RFA PFB esters were used for confirmation and quantitation. For better sensitivity, these ions were divided into the following five retention time windows: (1) m/z 255

(palmitic) and m/z 269 (heptadecanoic), (2) m/z 283 (stearic), m/z 281 (oleic), m/z 279 (linoleic), and m/z 277 (linolenic), (3) m/z 301 (pimaric, sandaracopimaric, isopimaric, palustric and abietic) and m/z 299 (dehydroabietic), (4) m/z 301 (neoabietic) and m/z 333 (chloro-dehydroabietic), and (5) m/z 353 (tricosanoic) and m/z 367 (dichloro-dehydroabietic), so that only a few ions were monitored at a time.

3.0 RESULTS AND DISCUSSION

3.1 Formation of the PFB Esters

PFB esters of the RFA were easily formed by mixing the PFBBr reagent and the acids in acetone in the presence of potassium carbonate. For pure standards, the reaction completed in 30 min or less at room temperature. However, the presence of other effluent coextractives often slowed down the reaction. Thus, the derivatization was carried out at 60°C for 30 min. in order to ensure complete reaction. Longer reaction times did not produce higher yields of the esters in effluent samples.

3.2 GC resolution of the esters

Because of the similarity in molecular structures in many resin acids, complete GC resolution of these compounds either as free acids or as methyl esters could not be easily achieved even with high resolution capillary columns. For example, underivatized isopimaric, levopimaric and palustric acids coeluted on a 15 m DB-1 fused silica column [8]. The methyl esters of palustric and levopimaric acids also

coeluted on 10 m SE-30 and SE-54 columns, except at relatively low column temperatures [19]. However, their separation has been reported on a 25 m OV-17 column [20] and on the polar Silar 10C and BDS (butane-1,4-diol succinate) columns [19].

In this work, chromatographic resolution of the PFB esters of RFA has been attempted on capillary columns with three different stationary phases, namely, DB-17, DB-5 (or SPB-5), and DB-1 columns. Since separation of the PFB esters of palustric and levopimaric acids could not be achieved by any one of the above columns, levopimaric acid was subsequently excluded in our work. Resolution of the PFB esters of the other RFA by the above columns was depicted in Figures 1 to 3. All three columns were suitable for the analysis of the acids in pulpmill effluent samples. However, the PFB esters of stearic, oleic, linoleic and linolenic acids were better resolved on the more polar DB-17 column than the DB-5 and DB-1 columns. On the other hand, the two less polar columns provided better resolution for the esters of abietic and dehydroabietic acids, which were present in nearly all effluents. While the order of elution for many RFA PFB esters was the same with the above three columns, the esters of the four C18 fatty acids as well as those of abietic and dehydroabietic acids eluted in a different order on the DB-17 column as compared to that found for the DB-5 and the DB-1 column. Because of the lack of pure standards for the two individual chlorodehydroabietic acids in our laboratory, the order of elution for their PFB esters could not be ascertained. However, if the PFB esters of these two resin acids follow the same chromatographic pattern as their methyl esters, then, by analogy, the 14-chloro isomer would elute ahead of the 12-chloro isomer [21].

3.3 GC-ECD sensitivity

All RFA-PFB esters in our study had similar ECD sensitivity. The relative molar response factors of all esters were within a factor of three, with the isopimaric and neoabietic acid derivatives being the most and the least responsive compounds, respectively. The ECD was linear over a range from 50 to 1000 pg for each PFB ester injected. About 0.5 to 1.5 pg of the ester was required to give a signal to noise ratio of 10:1.

3.4 GC-MS data for the PFB esters of the RFA

Under electron impact conditions, the mass spectrum of a resin acid PFB ester was quite complicated. In each case, it consisted of many peaks below m/z 150 and a very strong PFB ion (m/z 181). Similar to the corresponding methyl esters, the following species were also very prominent for PFB esters of various resin acids, namely: m/z 121 (pimaric and sandaracopimaric acids), m/z 241 (isopimaric, palustric, and abietic acids), m/z 135 (neoabietic acid), m/z 239 (dehydroabietic acid), m/z 273 (chlorodehydroabietic acids) and m/z 307 (dichlorodehydroabietic acid) (see Table 2). The structures of these species were not elucidated in our work but they were believed to have arisen from the same fragmentation patterns as postulated for the methyl esters of the same resin acids [22]. Contrary to the methyl ester of a resin acid, the relative abundance of the molecular ion for the corresponding PFB ester was much lower (6 to 30 %). In addition, the following characteristic ions, $(M-C_6F_5CH_2)^+$ and $(M-C_6F_5CH_2-CO_2)^+$,

were also observed at lower intensities for some of the resin acid PFB esters. For the PFB ester of each fatty acid, the base peak in its mass spectrum was invariably the PFB ion (m/z 181). The $(M-C_6F_5CH_2)^+$ ion was generally weak and the molecular ion was absent in all but one case (Table 2).

The NICI mass spectra of the PFB esters of RFA using hydrogen, methane, and isobutane as reagent gases were also examined. In all cases, the molecular ion was not observed and the base peak was always the $(M-C_6F_5CH_2)^-$ ion. Since the latter ion is abundant and characteristic of the parent compound, it is therefore useful for identification and quantitation of RFA. Aside from the $(M-C_6F_5CH_2)^-$, $(M-C_6F_5CH_2+1)^-$, and $(M-C_6F_5CH_2+2)^-$ ions, no other ions of relative abundance over 10% existed in the NICI mass spectra. The absence of the pentafluorobenzyl anion (m/z 181) was consistent with those observed for the PFB esters of prostaglandins [23] and some phenoxy acid herbicides [24].

Among the three reagent gases tested, hydrogen was chosen for routine analysis. Although the overall sensitivity was lower by a factor of three or less with hydrogen, it did not contaminate the ion source as readily as the other two gases and thus the response factors could be maintained for an extended period of time in routine analyses. Since the sensitivity of EC-NICI under SIM mode was similar to an ECD for the detection of the PFB esters, the NICI technique was extremely useful for the confirmation and quantitation of RFA in effluent samples as described later. EI-MS, on the other hand, had much less potential applications because of lower overall sensitivity and the lack of an abundant characteristic ion for some RFA PFB esters.

3.5 Extraction, cleanup, recoveries and detection limit

In the literature, solvent extraction at pH 2-3 [9,10] and XAD column extraction at pH 9-10 [1] are the two major approaches for the recovery of RFA in effluent samples. In our work, the simpler and more rugged solvent extraction technique using methyl tert.-butyl ether (MTBE) as described by Voss et al. [20] was employed. Although our results indicated that this procedure provided virtually the same recovery of all the RFA at pH 2, 6, and 10, extraction was preferably carried out at a pH between 6 and 10 as the extracts in those cases contained smaller amounts of non-RFA coextractives. The use of dichloromethane on pulpmill effluents would generally cause emulsion and foaming in the extraction steps, thus losses of the organics could occur. Using a less polar solvent such as hexane would not produce any emulsion, yet the recovery of the resin acids were found to be reduced to 60 % or less.

In order to monitor any losses of the organic acids in the entire analytical procedure, a known amount of tricosanoic acid was spiked to the effluent sample prior to extraction. This acid was chosen as a surrogate since it was not detected in pulpmill effluent in any significant amount and also because of its PFB ester did not coelute with other resin acids and coextractives in the final analysis. A less commonly available compound, O-methylpodocarpic acid, was also used as a surrogate for RFA analysis by some workers [25,26]. However, it should be noted that the PFB ester of this surrogate has a retention time very close to that of dehydroabietic acid when chromatographed on either a DB-5 or a DB-1 column, thus causing incomplete resolution.

To minimize interferences from other sample coextractives, a silica gel cleanup step was included. All PFB esters of the acids in this work were quantitatively removed from the column by the 25:75 (v/v) DCM/PE mixture.

The recoveries of RFA were obtained by replicate (n=7) analyses of fortified samples of a final effluent with a low RFA blank. As shown in Table 3, recoveries of all acids at 1000, 100, and 10 µg/L levels were close to quantitative. It should be pointed out that the recoveries of palmitic, heptadecanoic, stearic, oleic, linoleic as well as dehydroabietic acids were blank subtracted. Also, the recoveries of two fatty acids (Table 3) at 10 µg/L could not be reliably obtained since their blanks were a few times higher than the spiking level. The single-laboratory precision (coefficient of variation) of the procedure was between 2 and 3% at 1000 µg/L, 5 and 8% at 100 µg/L, and 8 and 11% at 10 µg/L.

For routine ECD analysis, the estimated method detection limit was 1 µg/L based on a 25 mL effluent sample and a concentration factor of 10. Further improvement of the method detection limit, if required, can be achieved by using a higher concentration factor through a larger sample size and/or a smaller final volume.

3.6 Application to pulpmill samples

The present analytical procedure was applied to the analysis of many effluent samples collected outside of a few Ontario and Quebec softwood bleached kraft mills. In many cases, palmitic, stearic, oleic, linoleic, abietic and dehydroabietic acids at high µg/L levels

were found. In addition, most of the other resin acids at lower concentrations were also detected, although the chlorinated dehydroabietic acids were less commonly found. During the development of this method, the PFB ester procedure was compared with the methyl ester procedure using split effluent extracts. Although both methods gave similar results for RFA at high levels, the PFB ester-ECD method was undoubtedly more sensitive and reliable than the methyl ester-FID method for the determination of low levels of RFA in final effluents. In many instances, analytically and environmentally significant amounts of RFA though undetected by the methyl ester method were unequivocally determined by our new procedure.

Examples of the RFA concentrations found in some typical softwood kraft mill final effluents are given in Table 4. Among the effluents that we had examined, sample A was one of the few cases that the chlorinated dehydroabietic acids were found at significant levels. The EC-NICI-MS-SIM chromatogram of this sample is depicted in Figure 4 and it clearly demonstrates its sensitivity and selectivity for the detection of RFA in a complex sample. The MS results also confirmed the identities as well as the quantities of the RFA results obtained by an ECD. While effluents B (Figure 5) and C (Figure 6) were sampled from the same mill, the results shown in Table 4 were consistent with the fact that effluent B was collected at a site much closer to the mill than effluent C. The sensitivity of the PFB ester method was best exemplified by the analysis of effluent C as its total resin acid content was only about 74 µg/L and resin acids below 10 µg/L were readily detected.

ACKNOWLEDGMENT

The authors sincerely thank our colleagues in Environment Canada, Mr. Robert Hong-You of Wastewater Technology Centre and Ms. Dominique Duval of Water Quality Branch, Quebec Region, for the provision of the effluent samples.

REFERENCES

1. A.B. McKague, J.M. Leach, R.N. Soniassy, and A.N. Thakore, Pulp Pap. Can. Trans. Tech. Sect., 78:3 (1977) TR75.
2. C.C. Walden and T.E. Howard, Tappi, 60:1 (1977) 122.
3. C.C. Walden and T.E. Howard, Pulp Pap. Can., 82:4 (1981) T143.
4. I. Rogers, H. Mahood, J. Servizi, and R. Gordon, Pulp Pap. Can., 80:9 (1979) T286.
5. M.H. Priha and E.T. Talka, Pulp Pap. Can., 87:12 (1986) T447.
6. J. M. Leach, J.C. Mueller, and C.C. Walden, Pulp Pap. Can. Trans. Tech. Sect., 18:12 (1977) TR 126.
7. Abstracted from the Material Safety Data Sheets (MSDS) supplied by Helix Biotech Co. for resin acids and chlorinated guaiacols.
8. R. Gref, J. Chromatogr., 448 (1988) 428.
9. B. Holmbom, Paperi ja Puu, 62 (1980) 523.
10. V.E. Turski, M.E. Kuehnl, and B.F. Vincent, Tappi, 64:5 (1981) 117.
11. A.S.Y. Chau and K. Terry, J. Assoc. Off. Anal. Chem., 59 (1976) 633.
12. H.B. Lee and A.S.Y. Chau, J. Assoc. Off. Anal. Chem., 66 (1983) 1029.
13. H.B. Lee and A.S.Y. Chau, J. Assoc. Off. Anal. Chem., 66 (1983) 1023.
14. H.B. Lee, L.D. Weng, and A.S.Y. Chau, J. Assoc. Off. Anal. Chem., 67 (1984) 1086.
15. H.B. Lee, Y.D. Stokker, and A.S.Y. Chau, J. Assoc. Off. Anal. Chem., 69 (1986) 557.
16. S-Z. Sha and A.M. Duffield, J. Chromatogr., 284 (1984) 157.

17. T.M. Trainor and P. Vouros, Anal. Chem., 59 (1987) 601.

18. H.A. Moye and J.P. Toth, "Negative ion electron capture chemical ionization mass spectrometry of fluorinated pesticides derivatives" in "Applications of New Mass Spectrometry Techniques in Pesticide Chemistry" (1987) edited by J.D. Rosen, John Wiley & Sons, New York.

19. D.O. Foster and D.F. Zinkel, J. Chromatogr., 248 (1982) 89.

20. R.H. Voss and A. Rapsomatiotis, J. Chromatogr., 346 (1985) 205.

21. A.N. Thakore and A.C. Oehlschlager, Can. J. Chem., 55 (1977) 3298.

22. T-L. Chang, T. E. Mead and D.F. Zinkel, J. Amer. Oil Chem. Soc., 48 (1971) 455.

23. R.J. Strife and R.C. Murphy, J. Chromatogr., 305 (1984) 3.

24. J. Carron, unpublished results.

25. L. LaFleur, "Procedure for the analysis of resin and fatty acids in pulp mill effluents", Natl. Conc. Pap. Ind. Air Stream Improv., Tech. Bull. No. 501, 1986.

26. Anon., a procedure written by the Ontario Ministry of the Environment for the laboratories analysing resin and fatty acids under the MISA program.

LIST OF FIGURES

Figure 1. GC-ECD chromatogram of the RFA PFB esters as chromatographed on a 30 m DB-17 column. See Experimental for GC conditions. Peaks: 1 = palmitic, 2 = heptadecanoic, 3 = stearic, 4 = oleic, 5 = linoleic, 6 = linolenic, 7 = pimaric, 8 = sandaracopimaric, 9 = isopimaric, 10 = palustric, 11 = abietic, 12 = dehydroabietic, 13 = tricosanoic, 14 = neoabietic, 15 and 16 = chlorodehydroabietic, and 17 = dichlorodehydroabietic.

Figure 2. GC-ECD chromatogram of the RFA PFB esters as chromatographed on a 30 m DB-5 column. See Experimental for GC conditions. See Figure 1 for peak identification.

Figure 3. Total ion current chromatogram of the RFA PFB esters obtained under NICI conditions using hydrogen as a reagent gas and a 30 m DB-1 column. See Experimental for GC conditions. See Figure 1 for peak identification.

Figure 4. Hydrogen NICI-MS selected ion monitoring trace of the RFA PFB esters of effluent sample A.

Figure 5. GC-ECD trace of the RFA PFB esters of effluent sample B.

Figure 6. GC-ECD trace of the RFA PFB esters of effluent sample C.

TABLE 1

Some information for selected resin and fatty acids

RFA	MW	% Purity	96 h LC50 [1]
palmitic	256.43	99	NA
heptadecanoic	270.46	97	NA
stearic	284.48	99+	NA
oleic	282.47	99+	3.2 - 8.0
linoleic	280.46	99	2.0 - 4.5
linolenic	278.45	99	3.0 - 6.0
pimaric	302.46	85 - 90	0.7 - 1.2
sandaracopimaric	302.46	85 - 90	0.4
isopimaric	302.46	99+	0.4 - 1.0
palustric	302.46	90 - 95	0.5 - 0.6
abietic	302.46	90 - 95	0.7 - 1.5
dehydroabietic	300.45	99+	0.8 - 1.7
neoabietic	302.46	99+	0.6 - 0.7
chlorodehydroabietic	334.90	90 - 95 [2]	0.6 - 0.9
dichlorodehydroabietic	369.35	90 - 95	0.6 - 1.2

[1] All LC50 values, in mg/L, were determined for trout or salmon.

[2] Supplied as an approximate 1:1 mixture of the 12- and 14-chloro isomers.

TABLE 2

Mass number (m/z) and % relative abundance (in parentheses) of some characteristic ions observed for resin and fatty acid PFB esters under electron-impact conditions

Parent acid	$M^{+\cdot}$	$(M-181)^{+}$	$(M-181-44)^{+}$	Other
palmitic	436(0)	255(6)	--	181(100), 237(14)
heptadecanoic	450(0)	269(9)	--	181(100), 251(16)
stearic	464(0)	283(7)	--	181(100), 265(16)
oleic	462(0)	281(6)	--	181(100), 263(14)
linoleic	460(0)	279(19)	--	181(100), 261(5)
linolenic	458(3)	277(2)	--	181(100), 261(6)
tricosanoic	534(0)	353(4)	--	181(100), 335(14)
pimaric	482(6)	301(8)	257(23)	121(100), 181(95), 241(16)
sandaracopim.	482(8)	301(7)	257(15)	181(100), 121(90), 241(18)
isopimaric	482(11)	301(33)	257(31)	181(100), 241(66)
palustric	482(28)	301(0)	257(8)	241(100), 185(85), 467(43)
dehydroabietic	480(6)	299(0)	255(3)	239(100), 181(30), 240(29)
abietic	482(29)	301(59)	257(17)	181(100), 256(52), 241(39)
neoabietic	482(17)	301(4)	257(3)	135(100), 181(39), 148(30)
chlorodehy.	514(9)	333(0)	289(2)	273(100), 181(59), 275(48)
chlorodehy.	514(6)	333(0)	289(4)	273(100), 181(52), 275(44)
dichlorodehy.	548(10)	367(0)	323(6)	307(100), 181(82), 309(60)

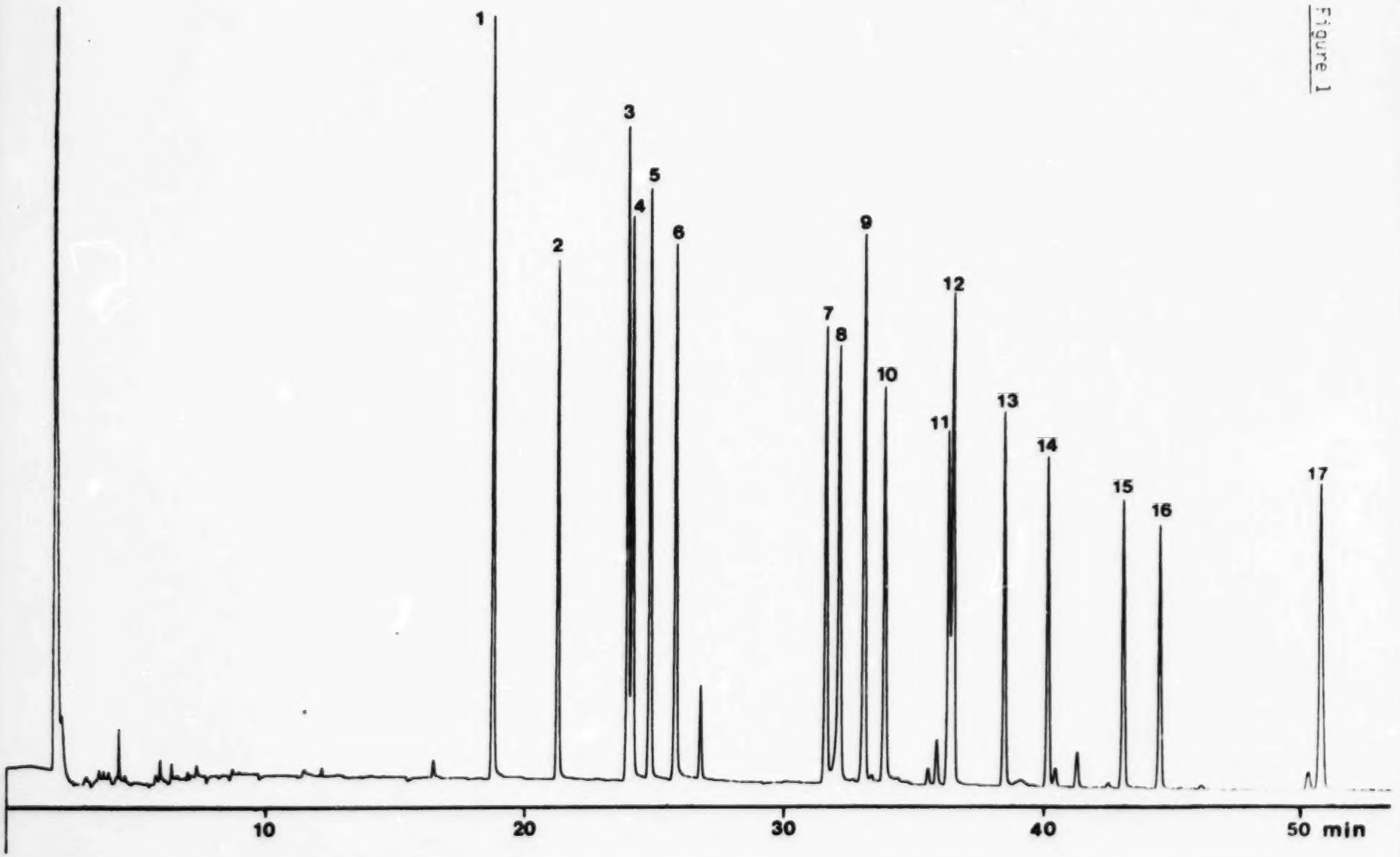

Figure 1

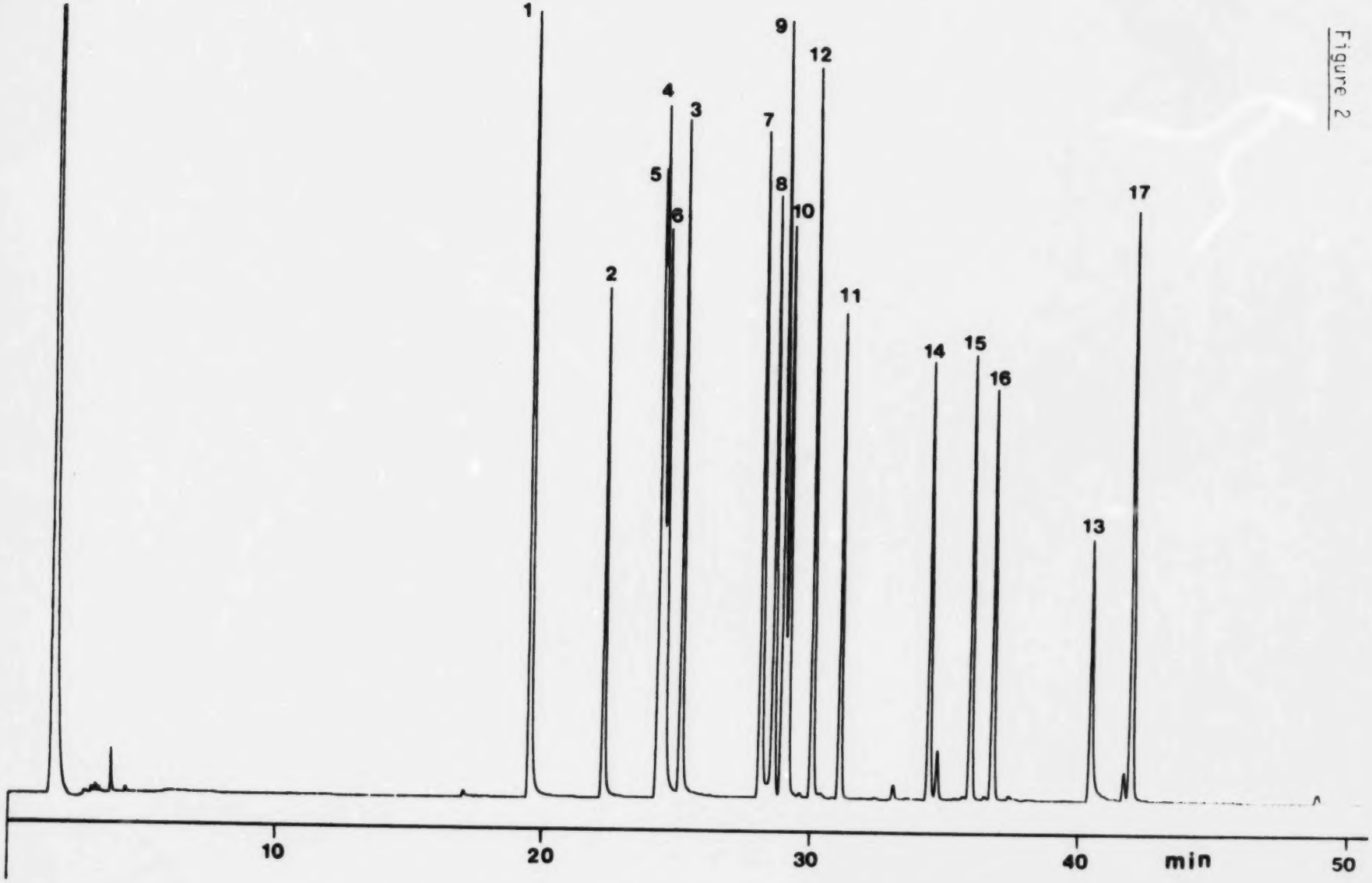

Figure 2

RIC
06/16/89 11:07:00
DATA: FA5 #1
CALI: FC43J15 #1
SCANS 800 TO 1300
SAMPLE: 0.5 UL X 25 PPM RFA-PFB STD MIX
CONDS.: 30M DB1 .32MM ID .25U 80-2->.140/10->>280/6--20 GC
RANGE: G 1, 5 LABEL: N -1,10.0 QUAN: A 1, 1.0 J 0 BASE: U 20, 3

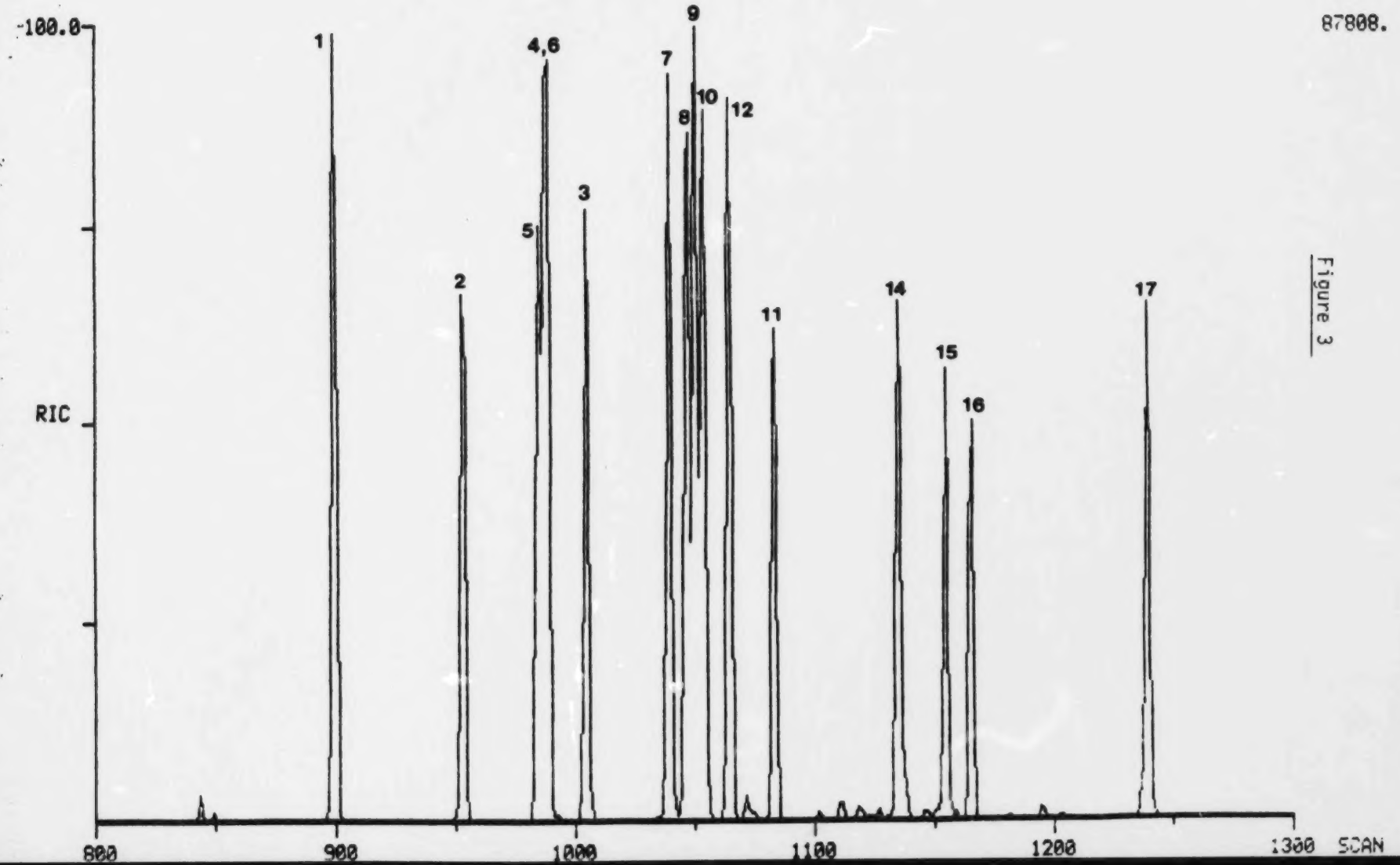

Figure 3

MIDRIC
06/16/89 16:05:00
SAMPLE: -VE CI SAMPLE A....MID SET UP
CONDS.: 30M DB1 .32MM ID .25U 80-2->.140/10->>280/6--20 GC
RANGE: G 1, 5 LABEL: N -1,10.0 QUAN: A 1, 1.0 J 0 BASE: U 20, 3

DATA: FA4B #1
CALI: FC43J15 #1
SCANS 700 TO 1100

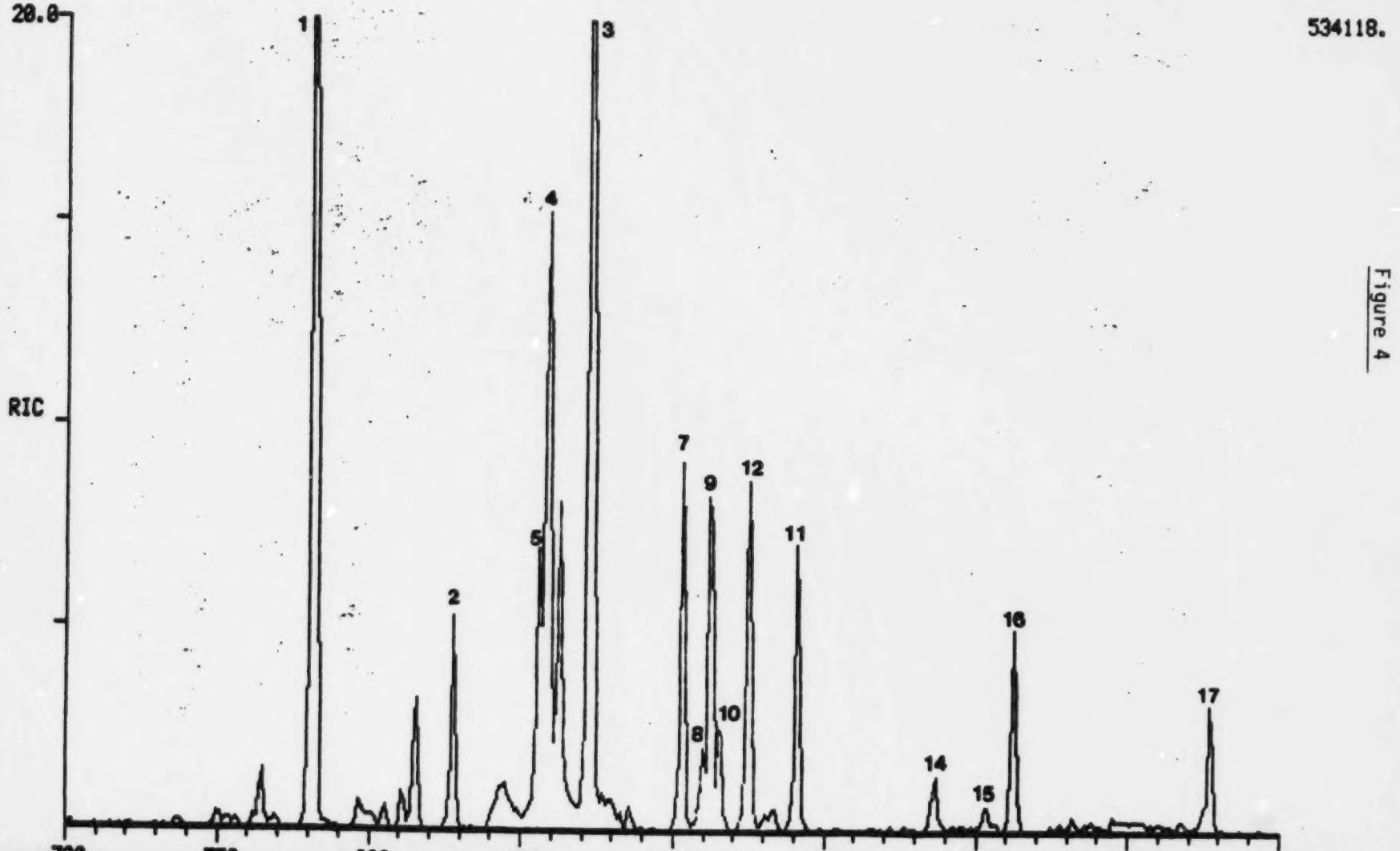

Figure 4

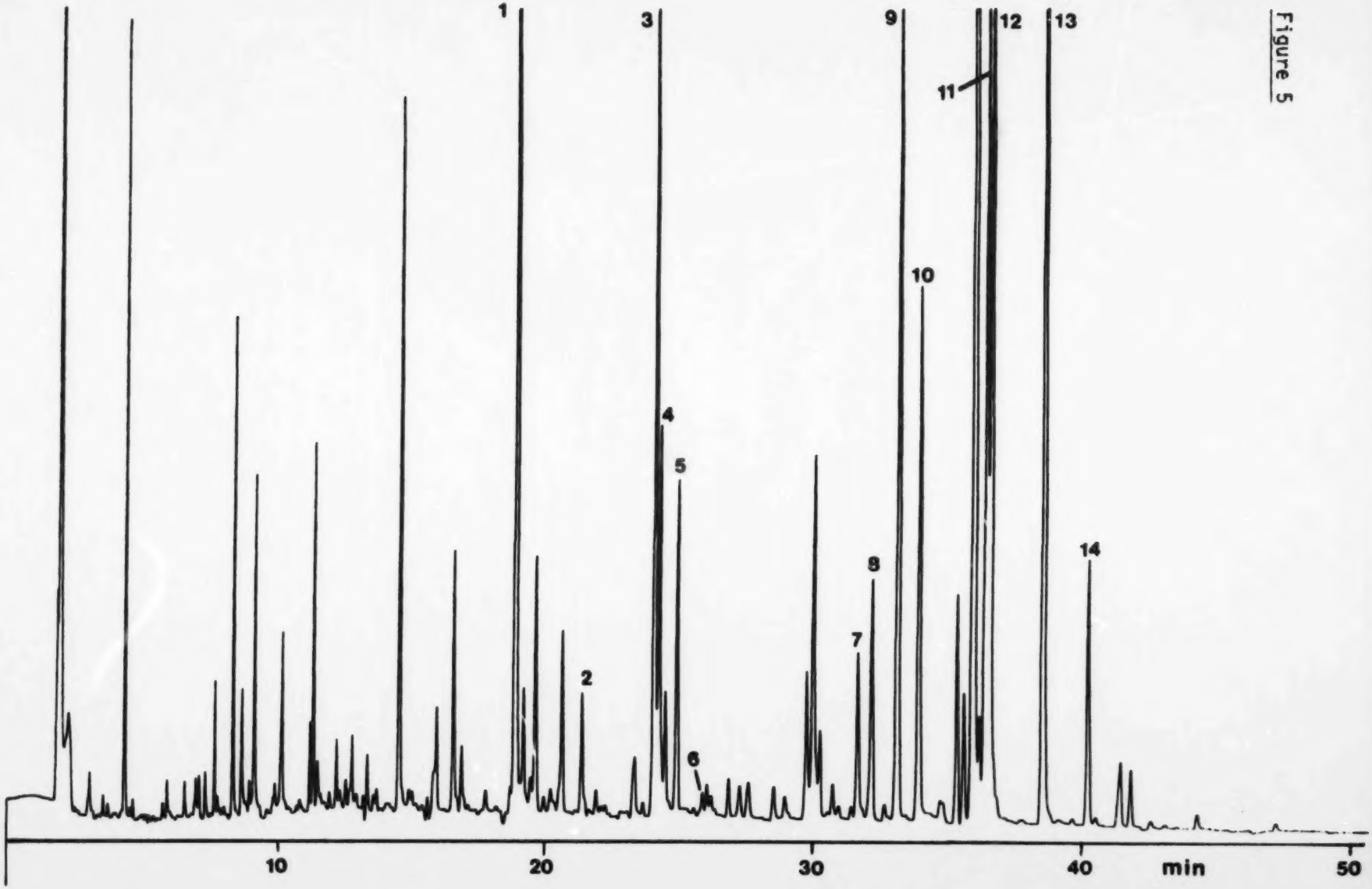

Figure 5

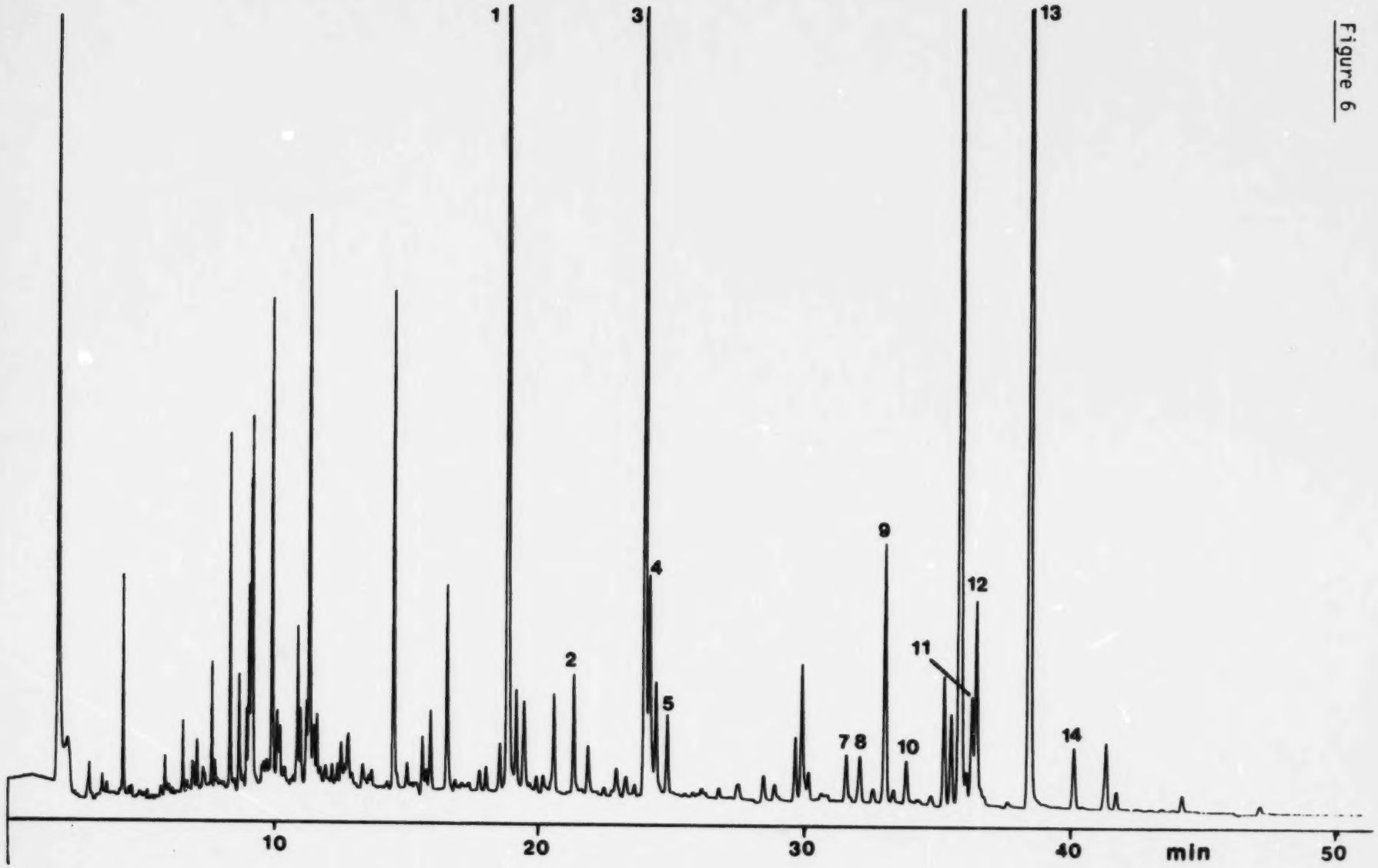

Figure 6